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(54) Low-Halogen Zinc Ferrite Pigments Production and Use

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Low-halogen zinc ferrite pigments production and use

ABSTRACT

A zinc ferrite pigment comprising, by weight, about 99.8 to 90% of ZnFe_2O_4 and about 0.2 to 10% of the component system $(1-x)\text{Al}_2\text{O}_3$ and $x\text{P}_2\text{O}_5$ wherein $0 < x < 1$ is produced by calcining a suitable mixture of compounds. The resulting pigments are of high color quality and are substantially halogen-free, rendering them especially useful industrially even as anti-corrosion pigments.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A zinc ferrite pigment comprising, by weight, about 99.8 to 90% of ZnFe_2O_4 , about 0.2 to 10% of the component system $(1-x)\text{Al}_2\text{O}_3$ and $x\text{P}_2\text{O}_5$ wherein $0.25 < x < 0.95$, and less than 30 p.p.m. of halogen.
2. A pigment according to claim 1 comprising, by weight, about 99.5 to 95% of ZnFe_2O_4 and about 0.5 to 5% of the component system $(1-x)\text{Al}_2\text{O}_3$ and $x\text{P}_2\text{O}_5$.
3. An organic binder, plastic, building material, paper, ceramic or anti-corrosion paint pigmented with a pigment according to claim 1.
4. In the production of a zinc ferrite pigment by calcining together a mixture of substantially equimolar quantities of zinc oxide and iron oxide or of precursors thereof which yield such oxides upon calcination at about 750 to 1000°C in an oxygen-containing atmosphere and thereafter cooling, the improvement which comprises adding to the mixture prior to calcination about 0.2 to 10% based on the total weight of compounds forming the component system $(1-x)\text{Al}_2\text{O}_3$ and $x\text{P}_2\text{O}_5$ wherein $0.25 < x < 0.95$ whereby the resulting pigment contains less than 30 p.p.m. of halogen and is of improved color quality.
5. The process according to claim 4, wherein cooling from calcination temperature down to about 400 to 500°C is effected slowly in the same atmosphere as during calcination.
6. The process according to claim 4, wherein the compounds forming the component system $(1-x)\text{Al}_2\text{O}_3$ and $x\text{P}_2\text{O}_5$ are finely particulate aluminum oxide and/or aluminum phosphates and/or

ammonium phosphates and/or free phosphoric acid or compounds yielding them on precipitation, drying and/or calcination.

7. The process according to claim 6, wherein the compounds forming the component system are added to the mixture to be calcined in the form of an aqueous suspension.

8. The process according to claim 6, wherein the compounds forming the component system are solids and intensively mixed with one another and then with the mixture to be calcined.

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Low-halogen zinc ferrite pigments production and use

The present invention relates to zinc ferrite pigments having a low halogen content which, in addition to the color-producing component ZnFe_2O_4 , include the colorless component system Al_2O_3 and P_2O_5 , to a process for producing these pigments and to their use.

10 Yellow zinc ferrites have been known for some considerable time. Although they may be inexpensively obtained, the products are attended by various disadvantages. Thus, they do not show any particular purity of color. Since they can only be produced by calcining together zinc oxide and iron oxide at temperatures in the range from 750°C to 1000°C in the presence of chloride catalysts (ZnCl_2 , HCl), as described in U.S. Patent No. 2,904,395, the zinc ferrites thus obtained contain corrosion-promoting quantities of halides.

Accordingly, the object of the present invention is to provide color-pure zinc ferrites which may readily be produced and which, in addition, do not have any of the above-mentioned disadvantages in regard to their practical applications.

20 Pigments which eminently satisfy all these requirements are zinc ferrites of which about 99.8% to 90% by weight and preferably about 99.5 to 95% by weight based on the weight of the pigment, consists of ZnFe_2O_4 and about 0.2 to 10% by weight and preferably about 0.5 to 5% by weight, based on the weight of the pigment, of the component system $(1-x)\text{Al}_2\text{O}_3$ and $x\text{P}_2\text{O}_5$ where x is greater than 0.25 and less than 0.95.

The zinc ferrite pigments according to the invention have halogen contents of less than about 30 ppm.



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A simple process had now been found for producing the zinc ferrite pigments according to the invention by calcining together equimolar or substantially equimolar quantities of zinc oxide and iron or starting materials yielding them at temperatures of from about 750°C to 1000°C in an oxygen-containing atmosphere,

preferably air, characterized in that, after intensive mixing with finely particulate aluminum oxide and/or aluminum phosphates and/or ammonium phosphates and/or free phosphoric acid and/or with components yielding aluminum oxide and/or phosphate on calcination in quantities of from 0.2% to 10.0% by weight and preferably in quantities of from 0.5 to 5.0% by weight, the starting materials - in the form of an aqueous suspension or in the form of a mixture of the solids components - are heated after filtration, washing, sedimentation or concentration by evaporation, normal drying or spray drying or directly in the form of solids after intensive mixing in air or in air enriched or depleted with oxygen or in pure oxygen in the absence of halide catalysts, calcined and the resulting calcine subsequently cooled normally or slowly in the same atmosphere or in an oxygen-enriched atmosphere to temperatures below about 400°C - 500°C and thereafter, as required, to room temperature.

The insoluble additives in the system $(1-x) \text{Al}_2\text{O}_3$ and $x \text{P}_2\text{O}_5$ may either be added as solids to the aqueous suspension or other suspensions or to the finely particulate solids or they may even be precipitated by the addition of a suitable salt, base or an acid solution at about 0°C to 100°C and preferably about 20°C to 80°C. For example aluminum hydroxides, aluminum oxide hydroxides or aluminum phosphates of various compositions may be precipitated by the addition of hydroxyl ions, meta-, pyro-, ortho- or other phosphate ions or their free acids to aluminum ions or compounds yielding aluminum ions.

Where free phosphoric acids or soluble phosphates are added, it is often best to concentrate the suspensions by evaporation to dryness in order to avoid any losses of phosphate.

The dried and powdered filtered material or the above-mentioned dry powder mixture or the evaporation

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residue is calcined in air, subsequently cooled and the calcine optionally ground. Instead of being carried out in air, calcination may be carried out in air slightly enriched with oxygen, but especially in oxygen-enriched
5 air to pure oxygen, without the optical properties of the pigments being significantly affected. As usual, there is a reciprocal relationship between the calcination time and the calcination temperature in the sense that calcination generally takes longer at low calcination
10 temperature and is quicker at high temperature.

The pigments according to the invention with their considerable improvement in color quality, with their change from brown-orange-yellow to more lemon-yellow hues, with their higher color saturation and their
15 greater brightness, are a valuable addition to the range of heat-stable, yellow pigments. The pigments may be used for pigmenting building materials, lacquers and dispersion paints, for coloring plastics and paper, for pigmenting ceramics and, in virtue of their low
20 halogen content, even as anti-corrosion pigments.

The invention is illustrated by the following Examples.

EXAMPLES

The examples set out in Table 1 were carried out
25 as follows:

In a 1/4 mole batch, 20.342 g of ZnO or corresponding quantities of solid, basic zinc carbonate or an industrially produced basic, zinc carbonate suspension and 60.265 g of Fe_2O_3 or corresponding quantities
30 of solid $\alpha\text{-FeOOH}$, solid $\gamma\text{-FeOOH}$, solid Fe_3O_4 or industrially produced $\alpha\text{-Fe}_2\text{O}_3$ -red, $\alpha\text{-FeOOH}$ -yellow, $\gamma\text{-FeOOH}$ -orange and/or Fe_3O_4 -black suspension are diluted with water to a final volume of 600 ml depending on the viscosity of the suspensions accumulating. It is also
35 possible to mix finely particulate and reactive solids of the above-mentioned components. Also, alkali, ammonium,

alkaline-earth metal hydroxide or carbonate may be added to aqueous solutions of zinc and iron(II)- and/or iron(III)- salts corresponding to the above-mentioned quantities of ZnO and Fe_2O_3 and the hydroxides, basic or normal carbonates precipitated used as starting material for the zinc ferrite pigments to be produced. In the 1-tests, no additive is introduced into the liquid suspensions or into the powder-air dispersion whereas, the 2-tests, the type and quantity of additive indicated in Table 1 is introduced and, in every case, the liquid or solid dispersion is intensively mixed for 3 minutes at 6000 r.p.m. in a mixing siren. Thereafter, the aqueous suspension is filtered under suction, washed free from salts with water where soluble salts are present and the filter cake is dried at 105°C . The additives which varied in their composition are shown in Table 1 as percentages of the final pigment. The nature of the solid or liquid additives is characterized by the indication $(1-x) \text{Al}_2\text{O}_3$ and $x \text{P}_2\text{O}_5$ with $0.25 \leq x \leq 0.95$. Thus $x = 0$ (a value outside the invention) would mean the addition of pure Al_2O_3 or compounds yielding it on calcination, $x = 0.5$ would mean the compound AlPO_4 or compounds yielding it on calcination, $x = 0.75$ would mean the compound $\text{Al}(\text{PO}_3)$ or compounds yielding it on calcination and $x = 1$ (a value outside the invention) would mean the quantities of any acids of phosphorus or thermally decomposable phosphates corresponding to pure P_2O_5 .

The dried and powdered filtered material or the above-mentioned dry powder mixture or the evaporation residue is introduced into a platinum or porcelain crucible in quantities of 5 g and then calcined in air for 10 minutes at the temperatures indicated in the individual examples in an electrically heated

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muffle furnace, cooled in air in the manner indicated and the calcine optionally ground.

The coloristic improvements in the pigments produced in accordance with the invention containing the

above-mentioned additive (2) by comparison with the additive-free (1) blank tests treated in otherwise exactly the same way are quantitatively assessed by objective color measurement in color transfers containing organic binders and colored with the ground calcines obtained. Pigment testing is carried out in the air-drying binder Alkydal^(R)F 48 (a product of Bayer AG) using a pigment volume concentration of 10%. To this end, opaque lacquer films are produced from the pigment and binder in a color grinding machine. After drying, the color values are measured in accordance with DIN 53 236, method A, and are converted into the CIELAB, C 2 degree color values according to DIN 6174. For the tests carried out without (1) and with (2) additives, Table 1 shows the color values H_{degree} , C^* , L^* as measured with a Hunter D 25 Lab. Colour Differenzmeter* and subsequently converted and also the differences ΔH_{degree} , ΔC^* and ΔL^* . In each case, the differences arise from the corresponding values of the additive-free samples (1) which are deducted from the color values of the additive-containing samples (2). For a positive ΔH_{degree} -value, the positive Δ -values of the additive-containing samples, in relation to the additive-free samples represent a desirable change in color from a dull brown-orange yellow to a bright lemon yellow with tinges of green. If the ΔC^* value is positive, there is an always desirable increase in color saturation and hence an increase in purity of color and, if the ΔL^* -value is positive, there is a desirable increase in the brightness of the color separation which means that a smaller addition of lightening, expensive titanium dioxide pigment is required for obtaining an equally bright separation.

Now, comparison of the tests carried out shows that, in every case, the addition of $(1-x)Al_2O_3$ and $x P_2O_5$ produces improvements in the color values. This is documented here by positive ΔH_{degree} , ΔC^* and

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* Trade Mark

△ *L values of the tests with additives (2) in relation to the additive-free (1) tests carried out in otherwise exactly the same way - so-called blank tests.

Legends to Table 1:

- 5 S = solid; Sn = suspension; C = concentration of the suspension by evaporation; Pn = precipitation; A.F. = after-precipitation.
1. Basic zinc carbonate suspension
 2. $\alpha\text{-Fe}_2\text{O}_3$, finely particulate, precipitated red iron(III) oxide (U.S. Patent 2,946,103).
 - 10 3. $\alpha\text{-FeOOH}$, finely particulate precipitated yellow iron-(III) oxide hydroxide (US Patent No. 1,368,748 or DOS No. 25 56 406) air oxidation process.
 4. "Zinkoxid"^(R) aktiv (Active Zinc Oxide^(R)), a product
 - 15 of Bayer A.G.
 5. $\alpha\text{-FeOOH}$, finely particulate, yellow iron(III)oxide hydroxide from the reduction of aromatic nitro compounds by iron in the presence of aluminum salts (German Patent No. 515,758).
 - 20 6. $\gamma\text{-FeOOH}$, finely particulate yellow-orange iron(III) oxide hydroxide (DAS No. 12 19 009).
 7. Fe_3O_4 , finely particulate, black iron(II)-iron(III)-oxide from the reduction of aromatic nitro compounds by iron in the presence of concentrated iron(II)salts;
 - 25 German Patent No. 463,773 or precipitation black (DOS No 26 18 058 and U.S. Patent 4,090,888)
 8. ZnO - "Grünsiegel"^(R) (Green Seal^(R)), 99.9 %, a product of Grillo A.G.

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- I = normal cooling in air
- 30 II = 10 minutes in O_2 at 600°C, followed by normal cooling in air
- III = 5 minutes at 800°C (in air) + 10 minutes at 700°C (in air) + 20 minutes at 600°C (in air) + 20 minutes at 480°C (in air), followed by normal
- 35 cooling.

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- IV = 5 minutes at 800°C (in air) + 10 minutes at 700°C
(in air) + 10 minutes at 600°C (in air) + 20
minutes at up to 480°C (in air), followed by
normal cooling.
- 5 V = 5 minutes at 800°C (in air) + 10 minutes at 700°C
(in air) + 10 minutes at 600°C (in air) + 30
minutes at 450°C (in air), followed by normal
cooling.

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Table 1: Production conditions and color values of the zinc ferrite pigments

Test No.	Components used		Addition		Calcin- ation	Cool- ing	Absolute		values		difference in relation to blank test		Halogen content [ppm]
	ZnO	Fe ₂ O ₃	x	(1-x)Al ₂ O ₃ +xP ₂ O ₅			H _d degree	C*	L*	ΔH _d degree	ΔC*	ΔL*	
1.1	ZnCO ₃ [Sn, ¹]	α-Fe ₂ O ₃ [S, ²]	none	-	825	IV	54.6	36.2	44.7	-	-	-	
1.2	"	"	x=0.50[S]	2	"	"	58.2	38.5	46.9	+3.6	+2.3	+2.2	
2.1	ZnCO ₃ [Sn, ¹]	α-FeOOH[S, ³]	none	-	900	II	59.5	40.3	49.4	-	-	-	
2.2	"	"	x=0.50[S]	2	"	"	62.2	41.9	51.5	+2.7	+1.6	+2.1	
3.1	ZnCO[Sn, ¹]	α-FeOOH[Sn, ³]	none	-	875	IV	62.1	42.7	51.6	-	-	-	
3.2	"	"	x=0.50[S]	1	"	"	63.2	43.1	52.7	+1.1	+0.4	+1.1	-
4.1	ZnCO ₃ [Sn, ¹]	α-FeOOH[Sn, ³]	none	-	925	V	60.8	41.3	50.3	-	-	-	
4.2	"	"	x=0.50[S]	2	"	"	63.8	43.8	52.9	+3.0	+2.5	+2.6	
5.1	ZnCO ₃ [S, ⁴]	α-FeOOH[Sn, ³]	none	-	900	IV	57.7	37.8	48.1	-	-	-	
5.2	"	"	x=0.50[S]	2	"	"	62.9	42.7	51.7	+5.2	+4.9	+3.6	20
6.1	ZnCO ₃ [Sn, ¹]	α-FeOOH[Sn, ³]	none	-	850	III	60.6	41.5	50.8	-	-	-	
6.2	"	"	x=0.50[A.F]	1	"	"	61.4	42.2	51.9	+0.8	+0.7	+1.1	
7.1	ZnCO ₃ [S, ⁴]	α-FeOOH[S, ³]	none	-	875	IV	58.2	37.7	48.1	-	-	-	
7.2	"	"	x=0.50[S]	5	"	"	60.6	40.3	50.5	+2.4	+2.6	+2.4	
8.1	ZnCO ₃ [S, ⁴]	α-FeOOH[S, ³]	none	-	875	IV	58.1	37.7	48.1	-	-	-	
8.2	"	"	x=0.50[S]	10	"	"	58.2	39.6	49.6	+0.1	+1.9	+1.5	
9.1	ZnCO ₃ [Sn, ¹]	α-Fe ₂ OOH[Sn, ⁵]	none	-	900	IV	58.6	38.1	48.1	-	-	-	
9.2	"	"	x=0.50[S]	2	"	"	64.5	43.1	52.3	+5.9	+5.0	+4.2	10
10.1	ZnCO ₃ [Sn, ¹]	α-FeOOH[Sn, ⁵]	none	-	850	I	58.7	36.7	47.8	-	-	-	
10.2	"	"	x=0.50[S]	2	"	"	62.8	39.4	50.3	+4.1	+2.7	+2.5	

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Table 1: Production conditions and color values of the zinc ferrite pigments - continuation

Test No.	Components used		Addition (1-x)Al ₂ O ₃ + xP ₂ O ₅	Calcination °C	Cooling	Absolute		values		difference in relation to blank test		Halogen content
	ZnO	Fe ₂ O ₃				x	%	H _{degree}	C*	L*	ΔH _{degree}	
11.1	ZnCO ₃ [Sn, ¹⁾]	α-FeOOH[Sn, ⁵⁾]	none	900	IV	58.6	38.1	48.1	-	-	-	-
11.2	"	"	x=0.75[S]	"	"	63.4	42.1	51.6	+4.8	+4.0	+3.5	-
12.1	ZnCO ₃ [S, ⁴⁾]	γ-FeOOH[S, ⁶⁾]	none	875	IV	57.8	37.8	46.6	-	-	-	-
12.2	"	"	x=0.50[S]	"	"	59.8	39.7	48.0	+2.0	+1.9	+1.4	-
13.1	ZnCO ₃ [Sn, ¹⁾]	Fe ₃ O ₄ [Sn, ⁷⁾]	none	900	III	60.2	36.4	46.7	-	-	-	-
13.2	"	"	x=0.50[S]	"	"	62.3	36.5	47.5	+2.1	+0.1	+0.8	-
14.1	ZnO[S, ⁸⁾]	α-FeOOH[Sn, ³⁾]	none	925	V	62.9	43.7	52.1	-	-	-	-
14.2	"	"	x=0.5[S]	"	"	65.2	45.2	53.7	+2.3	+1.5	+1.6	<10
15.1	ZnSO ₄ /Na ₂ CO ₃ [Pn]	FeSO ₄ /Na ₂ CO ₃	none	875	IV	51.6	24.7	39.7	-	-	-	-
16.1	ZnCO ₃ [Sn, ¹⁾]	α-FeOOH[Sn, ³⁾]	x=0.5[S]	"	"	54.2	26.9	42.1	+2.6	+2.2	+2.4	-
17.1	ZnCO ₃ [Sn, ¹⁾]	"	none	875	IV	57.5	38.0	47.9	-	-	-	-
17.2	"	"	x=0.33[C]	"	"	63.3	43.3	52.1	+5.8	+5.3	+4.2	-
18.1	ZnCO ₃ [Sn, ¹⁾]	α-FeOOH[Sn, ³⁾]	none	875	IV	57.5	38.0	47.9	-	-	-	-
18.2	"	"	x=0.50[C]	"	"	63.1	43.3	52.0	+5.6	+5.3	+4.2	10
19.1	ZnCO ₃ [Sn, ¹⁾]	α-FeOOH[Sn, ³⁾]	none	875	IV	57.5	38.0	47.9	-	-	-	-
19.2	"	"	x=0.75[C]	"	"	62.3	42.4	51.3	+4.8	+4.4	+3.4	-
20.1	ZnCO ₃ [Sn, ¹⁾]	α-FeOOH[Sn, ³⁾]	none	875	IV	57.5	38.0	47.9	-	-	-	-
20.2	"	"	x=0.83[C]	"	"	60.1	42.2	50.7	+2.6	+4.2	+2.8	-
			none	875	IV	57.5	38.0	47.9	-	-	-	-
			x=0.95[C]	"	"	59.8	42.0	50.7	+2.3	+4.0	+2.8	-